A Study on Porous Silicon Gas Sensors: Metal Oxide Depositions to Organic Materials

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A Study on Porous Silicon Gas Sensors: Metal Oxide Depositions to Organic Materials

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LIST OF SYMBOLS OR ABBREVIATIONS

DFT	Density Functional Theory.
HOMO	highest occupied molecular orbit.
HSAB	hard/soft acid/base.
IHSAB	inverse hard/soft acid/base.
LUMO	lowest unoccupied molecular orbit.
MFC	mass-flow-controller.
PL	polylysine.
PMMA	poly(methyl methacrylate).
PPy	polypyrrole.
PS	porous semiconductor.
PSi	porous silicon.
sccm	standard cubic centimeters per minute.
SEM	scanning electron microscope.
UHP	ultra-high purity.
VOC	volatile organic compounds.
XPS	X-ray photoelectron spectroscopy.

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SUMMARY

This paper has two main topics. The first topics covers the detection of volatile organic compounds with porous silicon (PSi) sensors. The second part explores the possibility of using conducting polymers as coatings for the PSi sensors as a catalyst for CO and CO_2 detection.

Porous semiconductor materials have been sought after as volatile organic compound gas sensors due to their optical properties. However, the optical sensors have a major flaw in their inability to distinguish different gases. Additionally, optical porous semiconductor sensors are overly sensitive to environmental factors, demising their ability to be used in an industrial setting. Therefore, in this project, we seek to explore methods using conductometric porous silicon sensors, potentially solving the drawbacks of optical sensors. Additionally, we seek to use the data collected during this period to construct a better understanding of the interaction of gases and porous semiconductor materials, expanding on the inverse hard/soft acid/base theory.

Another flaw of porous semiconductor sensors is that they rely on the competing precesses of chemisorption and physisorption. If a gas is both physically and chemically inert, then the sensor will fail to detect the gas. However, certain polymers have the capability of acting as a catalyst, triggering electron exchange between the gas and sensor, producing the signal needed for detection. Studies have shown polypyrrole as a effective catalyst for CO_2 detection. We wish to combine that with metal oxide deposits for studying CO_2 in the IHSAB model.

CHAPTER I

GENERAL INTRODUCTION

1.1 Porous Silicon Sensors

The discovery of silicon and other semiconductor material may be the single most important factor that has revolutionized technology in the 20^{th} century. Furthermore, advancements in nano-technology have allowed us to even further explore the properties of these materials. In particular, we have been able to develop methods of electrochemically etching nano-scale porous structures on bulk silicon semiconductors [1]. The intrinsic property of a semiconductor gives an easily changeable electric conductivity, while the porous structure opens the gateway for external environments to further alter its electronic state [1, 2]. These pores, ranging from a few nanometers in diameter to a couple hundred, are usually denoted by their size as nanoporous, microporous, or macroporous [1]. These structures greatly enhances the electrical sensitivity of these materials, enough to use as ppm level gas sensors [1, 3]. In addition, our lab group has further enhanced the sensitivity of the sensors by depositing nanoporous structures on top of a microporous base [2].

In particular, our porous semiconductor (PS) sensors are made from the fabrication processes already establish by previous studies done by out lab group [4, 2, 3, 5]. The wafer we choose is a p-type (1 0 0), boron doped silicon, with a resistivity of 1-20 $\Omega \cdot cm$. After initial cleaning, a silicon carbide insulating layer is deposited by plasma-enhanced chemical vapor deposition. Then 2x4 mm windows are created with photolithography methods and reactive ion etching. This will act as a mask for electrochemically etching the porous structure onto the wafer. The actual etching of the porous is done with a 1 M HF, and 0.1 M tetrabutylammonium perchlorate (TBAP), acetonitrile (MeCN) solution, with 36 mA/cm^2 of current for approximately 30 min. The result is a porosity of $50-80\%$ with micropore diameters of 0.8 to 1.5 microns and pore depths varying from 10-30 microns. In addition to

the micopoous structure, these porous themselves are then covered in nanopores. Finally, a 3000 Å gold contact is deposited by e-beam evaporation. A summary of the fabrication of our porous silicon (PSi) sensors is shown in Figure 1.1.

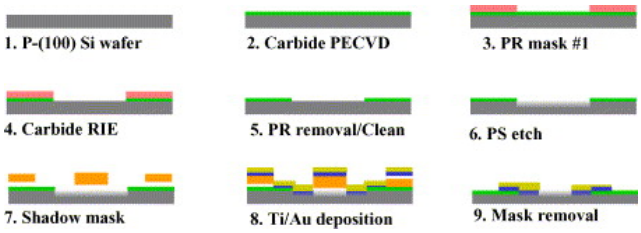


Figure 1.1: A overview of the fabrication process for the PSi sensors [4].

1.2 Theory Behind Porous Silicon Sensors

The fundamental concept we will be exploring in our sensor devices will be the inverse hard/soft acid/base theory (IHSAB), which is based on the more well known hard/soft acid/base theory (HSAB) [2]. In the HSAB theory, Lewis acids and basis are assigned a hardness based on their electrophilic properties. This generalizes the reaction of acids and bases to where hard acids and bases and soft acids and bases form ionic and/or covalent chemical bonds. However, hard acids do not bind strongly to soft bases and vice versa. Thus the closer two substances are in their hard/soft character, the stronger the formed chemical bond [6]. This was later correlated with the Density Functional Theory (DFT) by Pearson and Parr to validate the nature of the chemical process [7, 8, 9, 10]. The combination of DFT and HSAB theory, in turn, gave a physical background for the reaction of Lewis acids and bases.

Interestingly, as a result of the porous interface coated with nanostructures, gases interacting with specifically decorated PSi sensors obey the IHSAB model [2]. While traditional Lewis acid interaction interactions are characterized by HSAB theory, due to the physisorption properties of the nanoporous, gases interacting with the PSi sensors obey the IHSAB model [2]. Interacting with porous silicon, which is right in between hard and soft, acidic and basic gases donate or steal electrons (based on whether the gas is a acid or a base), decreasing or increasing the resistance dependent upon the silicon doping type. The PSi

sensor can then be coated with metal oxides to change their hardness, and the reaction of this new sensor with the gases scale with the difference in hardness (between the new PSi and the gas) [11, 2]. The larger the difference in chemical hardness between the analyte gas and the PSi sensors, the stronger the response; which lies in direct contrast to chemisoptive processes, where chemicals with similar hardness have stronger bonds to each other [2, 6]. Although the theory behind DFT and HSAB are fairly complete, the IHSAB model is still a active area of research. Previous works have completed a qualitative picture of how the gases and coatings affects the sensor when saturated, yet, a solid description of the actual process is still lacking. One of the goals of this study is to fill in the gaps needed to complete the theory. Initial ideas include studying the change in Fermi energy level of the sensor as gas saturates the pores.

1.3 Volatile Organic Compounds

Volatile organic compounds (VOCs) are, by definition, organic substances that share the feature of having high vapor pressure at room temperature. Spanning a large group of organic gases, VOCs include those with a significant health impact on humans, such as ones found in petroleum (benzene, toluene, and xylene). Traditional methods of VOC detection usually rely on the change in refractive index of a porous silicon (PSi) surface as the VOC gas fills up the pores [12, 1, 13]. While these methods did work and were able to detect very low concentrations of 10ppm [1, 14], their sensitivity to the external environment (such as humidity) was much too great [13]. Yet another drawback was their inability to distinguish gases; this is because their refractive index would change depending on how many of the pores were filled up, a property independent of the detected gas. However, unlike the shared optical properties PSi has with all gases, VOCs have very different chemical properties. Therefore, we are able to obtain different responses in contrast to inorganic gases. VOCs such as benzene and toluene are neither acidic nor basic, giving a minimum response to our sensors; yet, H_2S and CO, for example, are respectively hard and soft bases (with H_2S slightly harder than PSi and CO softer), whose response would dominate if mixed with the former two gases.

1.4 General Experimental Methods

The methods we will be using follow the same basic procedures given by Gole et al. in 2010 [2]. Our sensors are created by electrochemically etching a nanoporous structure on a mircoporous PSi array. The edge of each individual sensor is then coated with gold, for use as contacts. We then set probes on each side of the sensor, where the gold contacts are, and measure the resistance. First, we purge the sensors with ultra high purity (UHP) N_2, to remove any contaminants that could have attached to the sensor. After which, we turn on various gases and mixtures of gases in a given sequence, and study the change in resistance of the sensor. Furthermore, after a blank sensor has been run, we can coat it with metal oxides or apply various other treatments to change the response under a particular gas or combination of gases. This would allow us to compare results and obtain a better understanding of the interaction between the gases and PSi.

1.5 Polymer Deposition for Signal Enhancement

In addition to metal oxides, there are other methods of chemically, or physically, altering the sensitivity of our PSi sensors. One of the earlier approaches our group has tried is the nitration of the deposited metal oxides [15]. Although promising, such a method still focuses on the enhancement of signals, dismissing the possibility of detection for a wider variety of gases or selectivity in gas detected. Other studies have shown that certain conducting polymers, such as Poly(methyl methacrylate) (PMMA) [16] or Polypyrrole (PPy) [17] have the ability to grant PS sensors the ability to detect VOCs and CO_2, gases we are unable to confidently detect with current methods. In addition, we will visit idea of using polylysine to create sensors with selectivity towards certain gases. More will be explained in Section 3.2 and much of Chapter 4.

CHAPTER II

METAL OXIDE DEPOSITION

2.1 Metal Deposits and the IHSAB Theory

A chemical reaction where a electron exchange between the two reactants results in a covalent bond can be explained by the Lewis acid-base theory. The chemical that donates the electrons is a base, while the one accepting electrons will be an acid. Some common Lewis acids and bases are listed in Table 2.1. However, remember that the categorization of acid or base depends on the chemical reaction, not the reactant.

	Hard	Borderline	Soft
Acids	H^+, Li^+, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Cr^{2+}, Cr^{3+}, Al^{3+}, SO_3, BF_3, Sn^{4+}, Ti^{4+}	Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, SO_2, BBr_3, Sn^{2+}, NO_2, NO^+	Cu^+, Au^+, Ag^+, Tl^+, Hg_2^{2+}, Pd^{2+}, Cd^{2+}, Pt^{2+}, Hg^{2+}, BH_3
Bases	$F-$,OH^-, H_2O, NH_3, CO_3^{2-}, NO_3^-, O_2^-	NO_2^-, SO_3^{2-}, Br^-, N_3^-, N_2, H_2S, C_6H_5N, SCN	$H-$, R^-, CN^-, I^-, CO, SCN^-, R_3P, C_6H_6, R_2S

Table 2.1: A list of common acid and bases categorized by their hardness and softness.

More recent developments in the Lewis acid-base theory utilizes components of density functional theory (DFT). The chemical reaction of an acid and base can be described by the hybridization of their molecular orbitals, calculated via DFT [9, 10]. This also introduces the concept of the hard/soft acid/base (HSAB) theory. If the chemical hardness, defined as the energy difference between the lowest unoccupied molecular orbit (LUMO) and the highest occupied molecular orbit (HOMO), is comparable among the acid and base, then the resulting chemical would be more stable [6, 7]. If the difference in the chemical hardness of the acid and base is large, the resulting chemical would be unstable. In summary, hard acids like to interact with hard bases, and soft acids with soft bases. The HSAB theory was

first proposed by Pearson in the 1960s, where the incorporation of DFT and the quantitative studies were done in the 1990s, after computers were useful for such calculations [10, 8].

Our PSi sensors rely on the physisorption of the gases, rather than chemisoprtion. The two are competing processes and thus the dominance of one would inhibit the other. Therefore, in order to maximize the process of physisorption, we decorate the sensor to inhibit chemisoprtion. This is usually done with the deposition of metal oxides. These metal oxides, when coated onto the PSi sensor, shift the chemical hardness of the sensor slightly towards that of the metal oxides. The increase in difference of chemical hardness between the sensor and the analyte gas will inhibit the chemisoprtion process and thus enhance physisorption, the source of our signal. For example, TiO_2, a hard acid, will increase the chemical hardness of the sensor, inhibiting the chemical reaction with softer bases, and thus increasing the signal for a soft base such as CO. Since the reaction signal strength is now stronger with the increase in difference of chemical hardness, which lies in contrast with the HSAB model, it is termed the inverse HSAB (IHSAB).

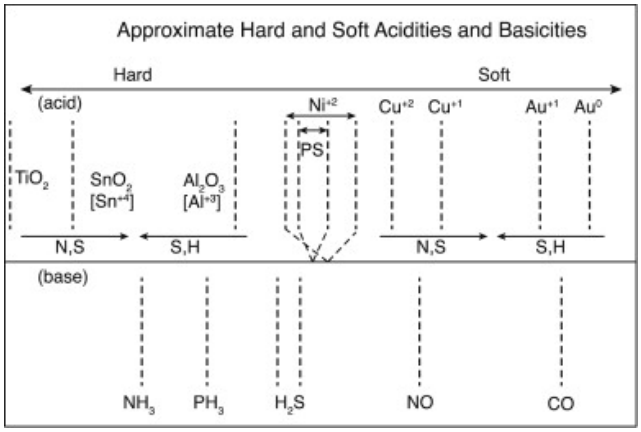


Figure 2.1: Hard/Softness and acidities/basicities estimates based on the resistance change of relative PSi sensors [18].

2.2 Methods for Metal Deposition

One of the convenient properties of PSi sensors is their ease of modification. As mentioned previously, certain metal ions, in the from of metal oxides (or hydroxides), have the ability to adjust the chemical hardness of our sensors, enhancing or diminish the signal of

corresponding analyte gases. Despite the modification being a inherently chemical process, all one needs to do for depositing material is to dip the sensor in aqueous solutions containing the metal ions. This process usually lasts from approximately 5 seconds to about a minute, depending on how much material we wish to deposit, followed by a cleaning process of 2 min in DI water and 2 min in methanol. The sensors are then allowed to dry overnight before used in testing for gases.

Depending on the metal ion we intend to deposit on the sensor, there are different solutions for treating the sensors. For example, most metals are stored as a metal chloride (M_xCl) aqueous solution. Placing the PSi sensors in the solution will cause the metal ions to attach to the porous structure, while the chlorine ions stays dissolved in water. The metal will subsequently form oxides (M_xO), and, in the case of group IIA, hydroxides ($M_x(OH)_2$). There are also other solutions used for depositing specific metal ions. Electroless gold ($Au^{0,+1}$) is stored in a potassium cyanide solution, and follows a similar process of oxidizing on the PSi surface.

To confirm that the metal oxides successfully latched onto the porous silicon structure, we preform x-ray photoelectron spectroscopy (XPS) to probe the substances on our sample. With our first prepared samples, there was not enough of the metal element to pick up a XPS signal out of the noise. Therefore, we proceeded to prepare samples where the senors were placed in the metal solutions for 10-40 min. Usually, this will result in a too much metal oxide begin deposited, causing cross-talk and worsening the detection signal. But for spectroscopy purposes, it helps prove that our method for treating the sensors does indeed place metal oxides on our PSi structure.

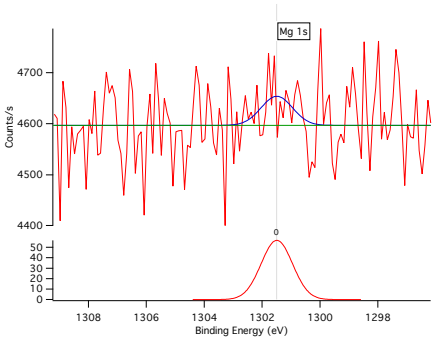
2.3 Group IIA Metal Oxides and Hydroxides

2.3.1 Introduction to group IIA metals

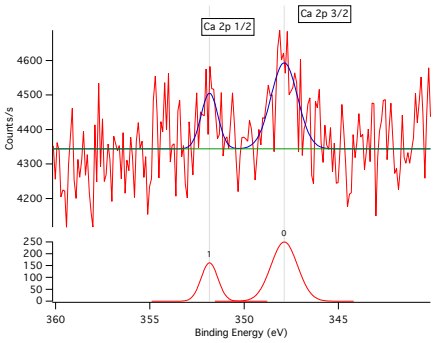
Group IIA metal ions are of particular interest because of their tendency to form hydroxides. These metal hydroxides are actually more stable than their metal oxide counterparts, a property no found in other elements of the periodic table. Normally, metal hydroxides

are alkaline, with $Mg(OH)_2$ being a weak base and the heavier elements being strong bases. However, since the dihydroxides are capable of donating a hydrogen ion, they could be Brønsted acids. In this study, we will also investigate the acidity of theses metal hydroxides, as they interact with PSi on a Lewis acid-base theory.

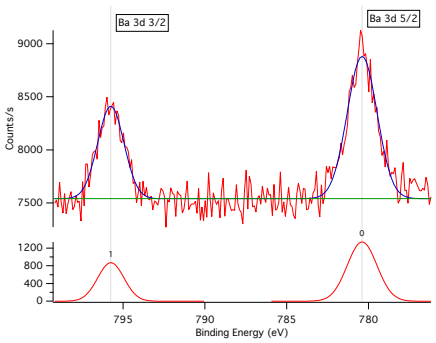
The sensors were treated by submerging them into the respective metal dichloride aqueous solution of 0.02M to 0.05M for 15 seconds. The metal ions, in contact with the PSi, would then proceed to form oxides and hydroxides. Though the metal oxides, hydroxides and the chlorides are all soluble in water, the latter is significantly more so. Therefore, traces of the group IIA metal oxides and hydroxides will be left on the PSi sensor. This is confirmed with XPS data of sensors submerged in the solution longer periods of time (10-30min).



(a) Mg



(b) Ca

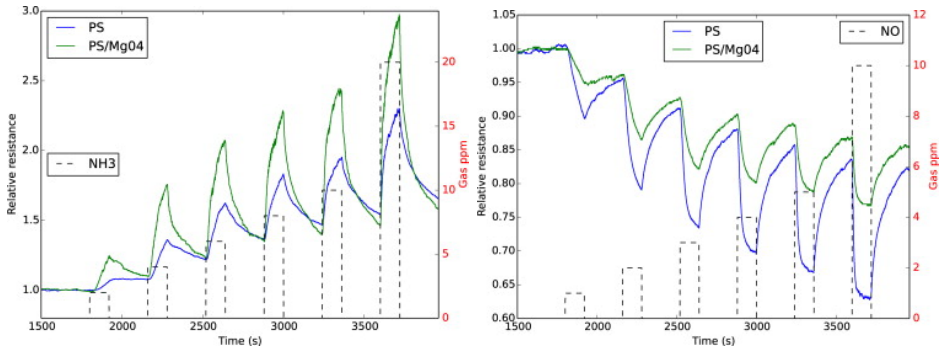


(c) Ba

Figure 2.2: XPS results for (a) Mg (b) Ca (c) Ba. This shows that the metal has been deposited on the sensor [5].

2.3.2 Mg^{2+} decorated sensors

After treating with Mg^{2+}, the PSi sensors have noticeably stronger response to NH_3 but a decrease in response to NO (Figure 2.3). This suggests Mg^{2+} has a chemical hardness more comparable to NO, implying that it is a soft acid in the IHSAB model. This falls in line with predictions of Lewis and Brønsted acids. The enhancement of signal increases with concentration from 0.02M to 0.04M. However, at a concentration of 0.05M and above, Mg^{2+} seems to decrease the signal. This may be that the abundance of Mg^{2+} on the porous structure has lead to cross-talk, and thus decreasing effectiveness.



(a) NH_3 (b) NO

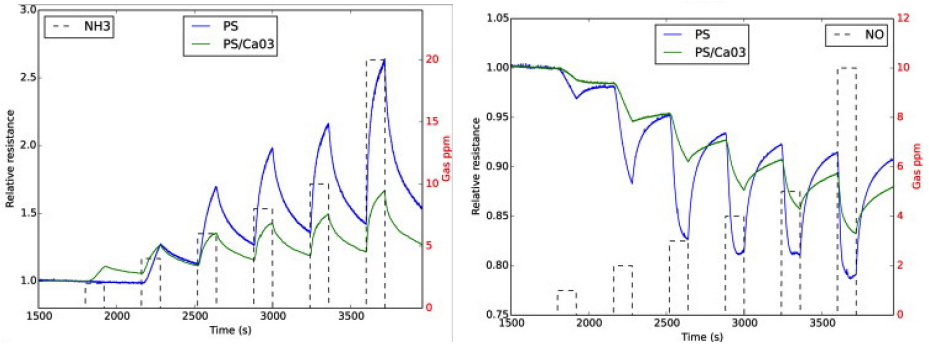
Figure 2.3: The resistance response of a p-type PSi coated with Mg^{2+} 0.04 mol solution solution when it's exposed to NH_3 and NO [5].

2.3.3 Ca^{2+} decorated sensors

Interestingly, the Ca^{2+} decorated sensors showed a decrease in response for both NH_3 and NO. Since ammonia is a hard base and nitric oxide is a soft base, this result cannot be explained by a shift in chemical hardness of the sensor. However, if the Ca modified the sensor to be more bases-like, this would inhibit the acid-base interaction of the sensors and lewis base gases, lowering the signal to all gases indiscriminately. This result was observed at all concentrations, with it being more profound at higher concentrations.

2.3.4 Ba^{2+} decorated sensors

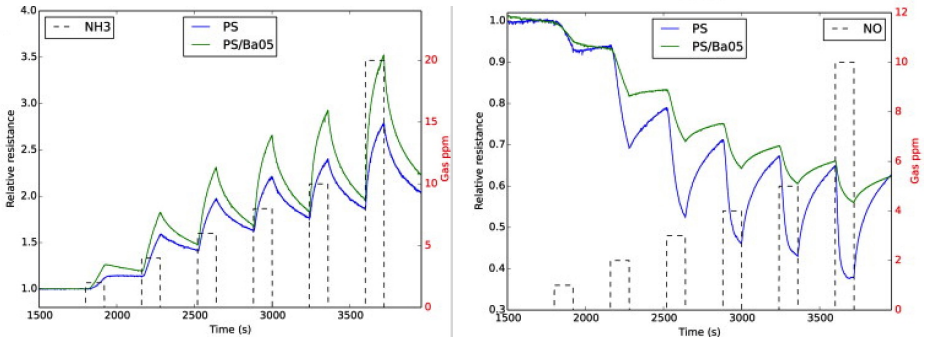
Finally, as for Ba, the treated sensor also showed diminished responses for both NH_3 and NO, at concentrations 0.02M through 0.04M. The signal for NH_3 also decreased noticeably



(a) NH_3 (b) NO

Figure 2.4: The resistance response of a p-type PSi coated with Ca^{2+} 0.03 mol solution solution when it's exposed to NH_3 and NO [5].

more dramatically than that of Ca^{2+} treated sensors. However, unlike Ca, which cause the NH_3 signal to decrease more with increasing concentration of Ca deposited, higher concentrations of Ba^{2+} did not reduce the the signal as much as lower concentrations. Additionally, for the 0.05M Ba^{2+} treated sensor, there seems to be a slight increase of response from NH_3. This result seems to be counter-intuitive of what the Lewis acid-base theory might suggest.



(a) NH_3 (b) NO

Figure 2.5: The resistance response of a p-type PSi coated with Ba^{2+} 0.05 mol solution solution when it's exposed to NH_3 and NO [5].

2.3.5 Conclusion

In conclusion, Mg^{2+} behaved as the soft acid predicted by the Brønsted acid model, consistent with Group IIA oxide formation. However, the conductometric measurements we

obtained from calcium and barium treated sensors suggest a decrease in their acidic character, consistent with theories that predict a stronger preference for hydroxides over oxides of calcium and barium relative to magnesium. Although metal hydroxides are classified as Brønsted acids, the donation of H^+ is irrelevant outside aqueous solutions. This further confirms that the IHSAB model operates under the Lewis acid-base theory and DFT.

CHAPTER III

VOLATILE ORGANIC COMPOUNDS

3.1 The Detection of Inorganic Gases in the Presence of VOCs

3.1.1 Introduction and methods

The classification volatile organic compounds (VOCs) encompasses a large amount organic substances both man-made and naturally occurring. A few of the most commonly found VOCs in the industrial setting are benzene, toluene (methylbenzene), and xylene (dimethylbenzene). The presence of these chemicals, combined with their highly volatile property, causes difficulties for many types of gas sensors. In particular, we are interested in the detection inorganic gases that often accompany these VOCs, and seek to confirm the functionality of our PSi sensors under a overwhelming presence of VOC gases.

Previous methods of VOC detection relied on the change in reflective index of PS sensors as the pores fill with gas [13, 14]. However, these sensors have the disadvantage of being unable to distinguish between inorganic gases and the VOCs. Yet, our sensors rely on the electrical properties of the PSi, instead of optical. Therefore, the minimal chemical interaction between the silicon and benzene group allows our sensors to operate under high concentrations of these VOC gases, maintaining their ability to detect low ppm-levels of inorganic gases.

A setup of our experiment is described in [19] and [20], with Figure 3.1. Ultra-high purity (UHP) nitrogen gas is pushed through the VOC liquid, bubbling the liquid and ensuring the vapor pressure of the VOC does not drop. The vapor, along with the N_2 is collected within the test tube containing the VOC, and can flow out trough another tubing controlled by a MKS mass-flow-controller (MFC). The concentration of the VOC gas can be calculated by the vapor pressure inside the test tube. In addition, there are two other tubings that

is connected to UHP N_2 and the analyte inorganic gas, independently, both controlled by their own MFC. This setup allows us to independently control the concentration of pure nitrogen, VOC gas, and the analyte inorganic gas independently, before they are all combined to approach the sensor. Our general approach is to first flow just the nitrogen and the VOC, and let the pores mostly saturate with the VOC. Then, under these conditions, turn on the flow of the inorganic gas. If we are able to obtain a signal in such case, then we know our sensors function under the presence of our chosen VOC gases.

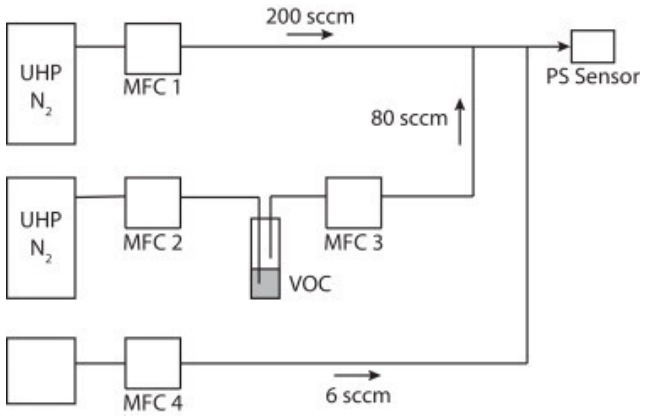


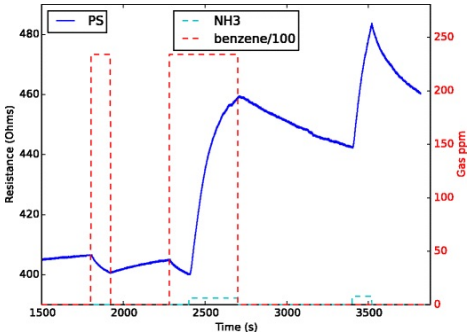
Figure 3.1: A schematic of our setup for detecting inorganic gases in the presence of VOCs. The gas flow controlled by mass-flow-controller 4 would be the analyte inorganic gas [20].

3.1.2 NH_3 detection in the presence of toluene, benzene, and xylene

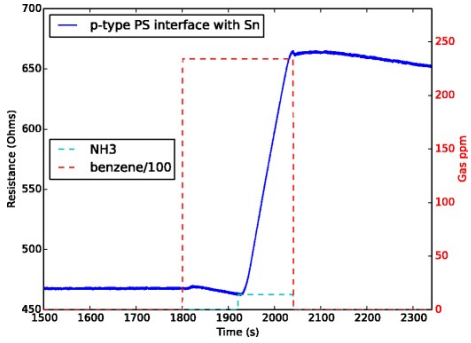
Both ammonia and benzene group compounds are biological products of bacteria and animals. Therefore, it is common to find both in the workplace of dairy, swine, and poultry industries. Though both of these substances are toxic, ammonia has a stronger adverse affect on the health of humans in such an environment. Thus, we seek to use our sensors as a selective detector of NH_3, mostly ignoring the presence of benzene and other VOC gases.

Experiment procedures mostly follow that outlined in the previous section. After purging the sensor with UHP nitrogen for 1500 seconds, extremely high concentrations (25000 ppm) of benzene is allowed to saturate the PSi for 120 seconds. Then, 6-14 ppm of NH_3 is added to the system for 120-240 seconds. It is during this period where we see the NH_3 signal dominate over benzene. Occasionally, there will be 120 second windows of just benzene or

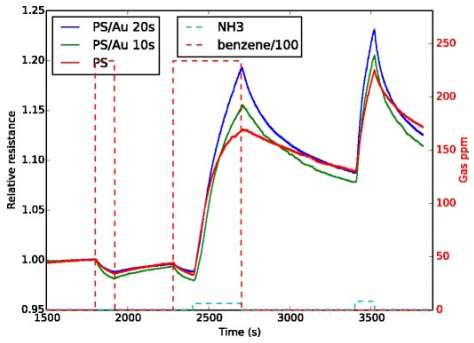
of just NH_3 to observe the effect these gases have on the sensor, without the presence of the other. The same process was repeated with benzene substituted for toluene or xylene. Similar results were obtained.



(a) Blank sensor



(b) Sn



(c) Au

Figure 3.2: Sensor response to NH_3 in the presence of benzene, where the sensors were (a) blank, untreated (b) treated with Sn (c) treated with Au [19]. Concentrations of NH_3 (denoted by the aqua colored dashed boxes) are (a) 6 ppm then 8 ppm (b) 14ppm (c) 6 ppm then 8 ppm.

In conclusion, if we can take the signal strength of gases as resistance change divided by gas concentration, we can then find the relative signal strength of NH_3 and the VOCs by tking the ratio. The results are shown in Table 3.1. Note that although the ratio is not infinite, the signal for the VOCs, especially benzene, is just barely above the noise level. Thus, it is hard to say if we are able to detect VOC gases on their own.

3.1.3 H_2S detection in the presence of toluene, benzene, and xylene

Another gas that is often present alongside VOCs is hydrogen sulfide (H_2S). H_2S is found as an impurity and contaminant in the extraction and refinement petroleum. It is also naturally occurring, in high concentration, at natural gas deposits. The ability to detect

	Toluene	Benzene	Xylene
Untreated sensor		65,000	
Sn decorated	1625	85,000	250
Au decorated		4000	

Table 3.1: A table listing the *lower bound* of the relative signal strength for NH_3 and VOCs [19].

H_2S in the presence of all the organic fumes in such a environment is crucial in maintaining the safety of said environments, as H_2S is highly toxic.

To begin, we tested the response signal of H_2S with sensors coated with TiO_2, SnO_2, NiO and Au_xO. All of the metals increased the signal response, but TiO_2 and Au_xO had a significantly stronger enhancement where NiO was abysmal in comparison. Following the IHSAB theory, this places hydrogen disulfide's chemical hardness close to NiO (show in Figure 2.1). Also, from the increase in resistance of the p-type sensors used, we can also conclude that H_2S behaves as a base when interacting with PSi.

The main portion of the experiment follows the setup and methods follow that outlined in Section 3.1.1. After placing the sensor in UHP N_2 for 1500 seconds, toluene was mixed with UHP N_2 at 500 ppm. The sensors would be mostly saturated with toluene gas by 240 seconds later, at which time, 21 ppm of H_2S was also introduced. The resulting signal from H_2S dominates over toluene, even at only a fraction of the concentration (Figure 3.3). The same procedure is repeated with benzene and xylene in place of toluene. Similar results were obtained, where the detection of H_2S far suppresses and response from the VOCs.

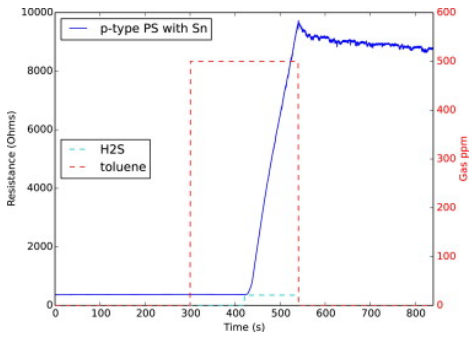


Figure 3.3: Tin coated sensor responding to H_2S in the presence of toluene [20].

We organize our results in the same fashion as we did with ammonia. Signal strength is found be the resistance change divided by concentration. How well we can detect H_2S in the presence of the VOCs is given by the ratio of the signal strengths. Results are shown in Table 3.2.

	Toluene	Benzene	Xylene
Relative Response	100,000	750,000	42,000

Table 3.2: A table listing the *lower bound* of the relative signal strength for H_2S and VOCs [20].

3.2 The Detection of VOCs with Porous Silicon Sensors

All the previous work done by our lab group is on the detection of inorganic gases. While we are able to obtain a small signal for the VOC gases, as shown in the previous section, it was at extremely high concentration. Even then, the signal is just barely above the noise level. Furthermore, we have no method for modifying the sensors, weather to enhance the signal or just study the properties of VOCs.

On the other hand, there are studies of VOC detection with the use of PS sensor [16]. It is primarily done with the use of conductive polymers, such as PMMA. And since out lab group has recently pick up the study of the use of such polymers, it would be interesting to revisit the detection of VOCs. In addition, the simultaneous use of sensors which are able to detect VOCs and ones which are not could help in the identification of mixed gases.

CHAPTER IV

CO AND CO_2 DETECTION

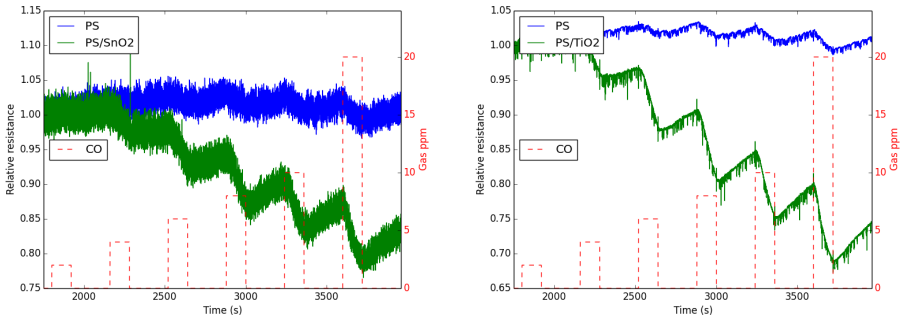
4.1 CO Detection with Metal Oxides

Under the Lewis acid-base theory, carbon monoxide is usually classified as a soft base. Yet, being a group IV oxide, it has amphoteric properties. In particular, we have found that CO gas interacting with our PSi sensors behave as soft acids, unless specially treated sensors are used. Additionally, CO is fairly inert in terms of an acid-base reaction. Therefore, for a blank, untreated PSi sensor, one is only able to achieve a fairly weak signal, if any at all. Yet, as a Lewis acid, CO interactions with PSi is still subject to the IHSAB model. Previous studies have shown a hard acid, such as Sn^{4+}, is able to enhance the signal for CO [2, 4].

In preparation for testing ploylysine (PL) coated PSi sensors, we revisited the detection of CO. We believe that some of the properties that CO share with CO_2, such as amphoterism, might give some insight on the detection of CO_2. To start, we ran CO with blank, untreated PSi sensors, of which, we discovered that only a few sensors from each wafer was able to pick up a signal out of the noise. We then proceeded to coat these sensors with TiO_2 and SnO_2. The results concur with previous studies [4], where Sn^{4+}, a hard acid, is able to enhance the signal (Figure 4.1a). Furthermore, we have found that Ti^{4+}, a even harder acid than Sn^{4+}, has even better capabilities of enhancing the sensing capabilities of CO (Figure 4.1b), which lie in agreement with the IHSAB model.

4.2 Polymer Coatings

There already exist studies that show certain polymers are capable of activating cites for gas and PSi to interact, such as PMMA for VOCs [16] and polypyrrole (PPy) for CO_2 [17]. For our study, we focused on the use of polylysinse for the detection of CO and CO_2,



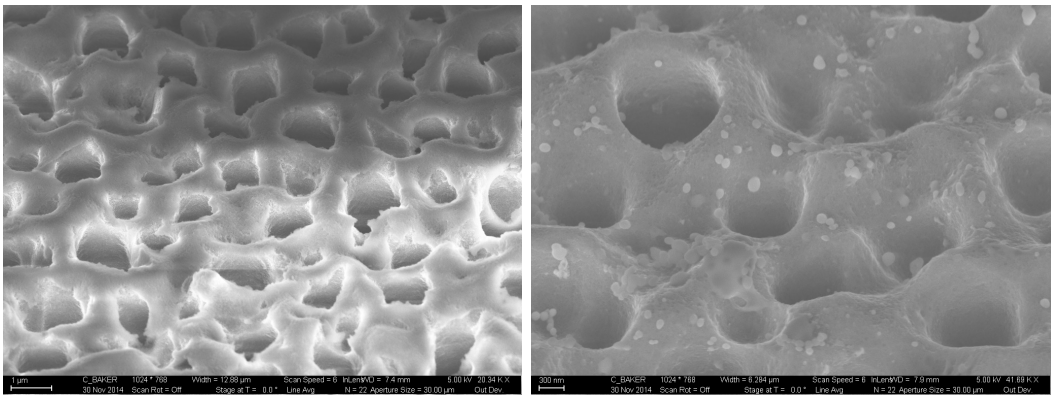
(a) SnO_2 (b) TiO_2

Figure 4.1: P-type sensor response to CO gas when coated with (a) SnO_2 (b) TiO_2.

although future work with other polymers and gases have been planed.

In order to coat our PSi sensors, we have a solution of poly-l-lysine (l denotes chirality), dissolved in DI water (0.1% w/v). We took two separate approaches for depositing the polymer onto the senor. One, we would place the PSi sensor in this PL solution, for 1 min, before rinsing the sensor with DI water. The other method was done after diluting the solution, 1:1 with DI water, before placing the sensor in the diluted solution for 2 minutes. Again, after the 2 minutes, the sensor was rinsed with DI water. For both methods, the treated sensors were allowed to dry overnight, and then placed on a hot plate of 80°C for 1.5 hours, to evaporate any remaining water trapped in the porous structure. After allowing approximately 30 minutes for the sensor to cool off, they were ready to be used for testing.

In order to confirm the successful deposition of polymer, we took scanning electron microscope (SEM) images of our sample (Figure 4.2). Images of samples with and without PL coatings were taken, at length scales of 1 to 0.1 microns. This also gives us a rough estimate of the size of the PL clustered deposited. Sadly, the metal oxide deposits are much smaller than the polymer. Thus, we are unable to see them at this length scale. Yet, other spectroscopy methods do prove successful deposition of both PL and metal oxides on the same sensor.



(a) blank (b) PL coated

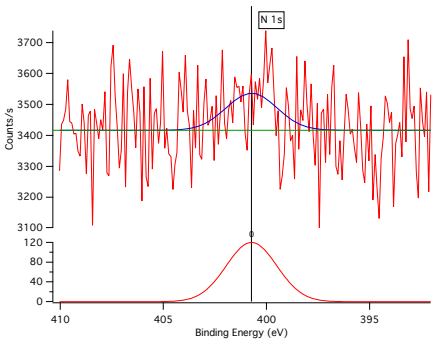
Figure 4.2: SEM pictures of (a) a blank untreated sensor, showing the porous structure and (b) polylysine deposits (the oval shaped blobs).

In addition to SEM, we also preformed XPS on the sensors to find further evidence that the PL successfully deposited onto the PSi sensors. In particular, we are looking for photoelectrons emitted from the nitrogen atom within the ploylysine molecular structure. As we see from Figure 4.3, after coating with PL, XPS shows a significant increase in the amount of nitrogen present from the sample. This further shows that the polymer has successfully latched onto the porous structure. Furthermore, this is still true in the combination with SnO_2, and other metal oxide coatings.

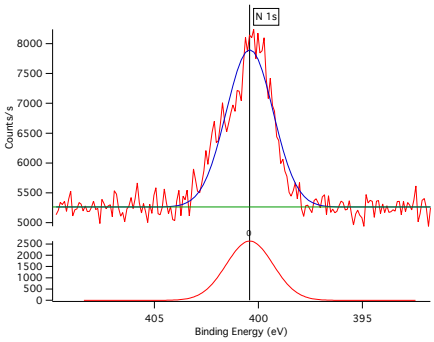
Finally, we wanted to also be sure that the polymer could be used in combination with metal oxides. Figure 4.4 shows the presence of Sn and Ti on a sensor that underwent metal oxide deposition after PL deposition. These are the different sensors than those in Figure 4.3, but the deposition methods are identical. Therefore, we assume PL is successfully deposited on these senors as well.

4.3 CO Detection with Polylysine

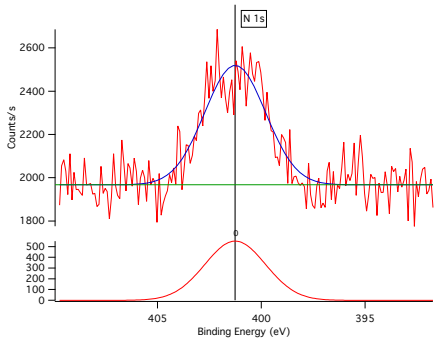
After finding untreated sensors that were able to detect CO, we precoded select these senors for further treatment. In particular, there were 4 sensors that had the capability to detect CO untreated. Two of them were coated with TiO_2 and SnO_2, individually. The other two were coated with PL using the two different methods described previously. After



(a) Blank sensor



(b) PL

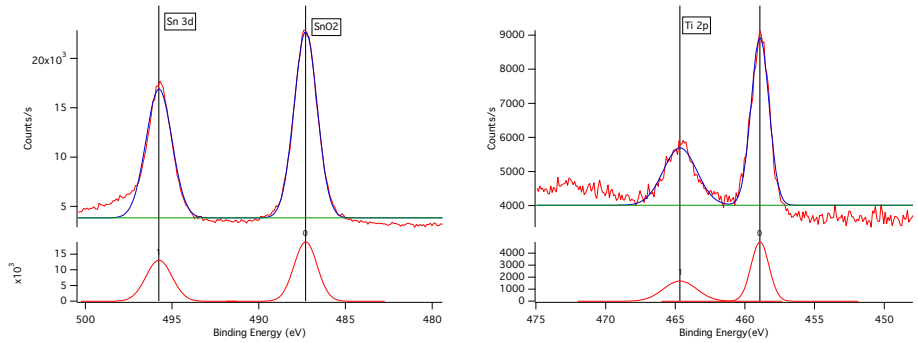


(c) Sn + PL

Figure 4.3: XPS results for (a) a blank, uncoated, sensor (b) a sensor coated with polylysine (c) a sensor coated with tin and polylysine. Here, nitrogen is used as indirect evidence for the presence of polylysine.

the two coated with metal oxides were run, they were subsequently coated with PL, using the diluted solution. The sensors initially coated with PL were subsequently coated with TiO_2, as it had a better signal enhancement over SnO_2 without PL.

Surprisingly, in contrast to what we theorized, coating the sensors with PL entirely killed the signal for CO. This was the case regardless if metal oxide was coated prior to PL. We tried both methods of coating, mentioned in the previous section. Yet, both gave the same result. However, even more intriguing is the fact that although the signal for other gases (NO, NH_3, H_2S) were also diminished, they did not totally disappear as CO did. Unintentionally, we may have discovered a method of adding selectivity to gases for our PSi sensors. This begs the question, do other polymers add selectivity for different gases? If so, this might be the most intresting discovery of this project. Further research on this topic is most likely to follow.



(a) Sn + PL (b) Ti + PL

Figure 4.4: XPS results for (a) a sensor coated with tin, and also coated with polylysine (b) a sensor coated with titanium. Shows that both metal oxides are valid enhancement materials, and can be used in combination with polylysine.

4.4 CO_2 Detection

Other groups have theorized that the N-H bond within certain polymers, such as polypyrrole (PPy), can act as activation cites for CO_2 gas to attach themselves to [17]. Once the gas starts interacting with the polymer, there would be indirect exchange of electrons between the gas and the porous silicon substrate. This allows us to measure a resistance change across the PSi sensor. Since PL is also a conducting polymer with a N-H bond, we thought that it would also be able to act as a catalyst to CO_2 detection. Sadly, as of the time this paper is written, we have yet to obtain a CO_2 signal from PL coated sensors.

Methods for deposition of PL follows that of metal oxides and is identical to the methods mentioned in Section 4.2. We also tested Au_xO depositions, as well as Au_xO and PL combinations. Theoretically, CO_2 is a hard acid. Thus, a soft metal oxide such as Au^+, when attached to the porous structure, should enhance the signal for CO_2. However, if the gas was not interacting with the PSi in any way to begin with, the result is still a null response. If more time and resources were available, it would be ideal to try other conducting polymers in addition to PL, with PPy being a promising candidate in particular.

CHAPTER V

FUTURE WORK

If time had allowed, there is so much more to explore, even with just data analysis alone. Almost all of what is presented here is the raw results of the experiment run. In addition to just plotting resistance changes, the data could be used for analysis on gas diffusion into the porous structure. Currently, we think that the various gases have unique diffusion rates based on their chemical and physical properties. A first derivative of our raw data would show the rate of response, which we will connect to the diffusion and saturation of the gas through the nano-structure. Such a study would shine light on the physical properties of both the gas and the PSi structure, and ideally lead to more theory development.

An interesting result that we did obtain, but were surprised by, was that coating the PSi sensors with PL almost selectively killed the signal for CO. Yet, short, unrecorded, data runs indicated that the signal for NH_3 and other gases, while weakened, did not disappear like that of CO. If follow up studies were to confirm this, we could have very well discovered a method for selective detection of certain gases. Just the prospect of being able to identify a gas alone definitely makes this a study worth pursuing.

Finally, there is literature that suggests polypyrrole is a conducting polymer with the ability of acting as activation cites for CO_2 [17]. We would very much like to try coating our sensors with the polymer and testing whether or not it would work with our experimental setup. In particular, there hasn't been any studies of the effectiveness of PPy in combination with metal oxides deposits. This could verify the chemical hardness of CO_2 as well as append organic materials to our IHSAB table.

CHAPTER VI

CONCLUSION

Porous silicon has the unique properties of electric and optical sensitivity, all while remaining reusable after repeated use. This makes them well suited as sensor material. Our group is particularly interested in the physical interactions of gases and nanoporous Si, modeling them as Lewis acid-base interactions following the IHSAB theory. Furthermore, by placing designated metal oxides (and hydroxides) on these sensors, we are easily able to modify the chemical hardness of the sensors, enhancing the signal for the detection of certain gases.

In parallel with IHSAB, we are developing a model that treats the interaction of PSi and these various gases similar to a p-n junction. The PSi has a band gap between it's valence band and conduction band. The analyte gases have a similar energy gap between their HOMO and LUMO. Both these gaps can be described as a chemical hardness, but also via Fermi levels of charge carriers. The flow of charge carriers can then be calculated by the relative Fermi energy levels of the PSi and the analyte gas. Furthermore, the Fermi level of the PSi can be modified by the metal oxides, which, in turn, enhance or limit the flow of charge carriers to and from the analyte gas. This theory should agreed with IHSAB and is still currently under development.

In the case of group IIA metal oxides, we have found that Mg^{2+} behaves accordingly to the Lewis acid theory and IHSAB. Mg^2+, in the form of MgO, behaves as a Lewis acid, with a chemical harness similar to NO. However, Ca^{2+} and Ba^{2+} behaved oddly, weakening the signal of both NO and NH_3 indiscriminately. We believe that these metals formed hydroxide sites that behaved like Lewis bases. The overall change from acidic to basic of the PSi sensor limited the interaction with the base-like gases, diminishing the signal overall.

Relying on the electrical properties of PSi, our sensors are more selective towards certain gases than porous semiconductor sensors that operate off infrared index of refraction. In this study, we have shown that our sensors are capable of detecting H_2S and NH_3 in the presence of benzene toluene and xylene. With the same date, we have a rough idea of the placement of these VOC gases in the IHSAB table. However, the signal is too weak to say with certainty. Future studies might include the direct detection of VOC gases, with the use of conductive polymer coatings.

In addition to VOC detection, conductive polymers can also be used for the detection of CO_2. Currently, we have tried poly-l-lysine coatings without any success. Our next step is to try ploypyrrole, which previous studies have shown to promising. In addition, we might be able to use polylysine for the selective detection of certain gases, something that would be very useful, but we are not sure of the actual implementation.

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